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# Rheokinetics and Effect of Shear Rate on the Kinetics of Linear Polyurethane Formation

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**In this article, the rheokinetics of polyurethane formation and the influence of shear rate on its kinetics have been studied. Two different linear polyurethane systems with 0% and 100% hard segments are examined in a cone and plate rheometer. The isothermal increase of viscosity during polyurethane formation has been measured at different shear rates and different temperatures and is modeled with an exponential function. The molecular weight vs. time curves and the reaction kinetic constants have been obtained for various shear rates and temperatures using gel permeation chromatography (GPC). It was concluded that kinetics of polyurethane formation is enhanced as the shear rate is increased. Phase separation is found to be responsible for irregularities in the viscosity build up due to formation of polyurethane with hard segments at high conversions. POLYM. ENG. SCI., 45:279–287, 2005. © 2005 Society of Plastics Engineers**

## INTRODUCTION

Thermoplastic polyurethanes (TPU) are extensively used as high performance elastomers and tough thermoplastics in a wide variety of industrial applications [1, 2]. Two common techniques for production of these polymers are based on reactive processing, including reaction injection molding (RIM) and reactive extrusion (REX) [3–6]. The important feature of reactive processes is that the polymerization and processing take place at the same time and the kinetics of reaction and the process conditions influence each other. In most cases, the monomers out of which TPU is produced are poorly miscible. Therefore, in the early stage of the reaction, mixing will enhance the apparent reaction velocity owing to an increased homogeneity of system and sometimes through enlargement of the contact surfaces of the immiscible monomers. During the reaction as well, the increase of

viscosity due to formation of high molar mass molecules can affect the flow pattern. The flow pattern and molecular diffusion, in turn, may influence the reaction rate and the final conversion in the reaction mixture. At the end of polymerization, the mobility of the functional end-groups and the catalyst might be improved by high shear rate conditions.

The kinetics of formation of polyurethanes has been studied by several authors [7–10]. The most common methods for data acquisition are titration, Fourier transform infrared (FTIR), adiabatic temperature rise (ATR), and gel permeation chromatography (GPC). The kinetic data are often reported neglecting the effect of shear rate for most polymerization systems including polyurethane formation. The influence of various reaction parameters such as temperature, catalyst type and concentration, and stoichiometric ratio of monomers have been well investigated during the kinetic studies. However, generally less attention has been paid to the effect of shear rate, if any, on the polymerization kinetics. The most relevant works on this aspect have been published on free radical polymerization. Kumar and Gupta [11] examined the rate of polymerization of styrene at different shear rates using a special dilatometer in which the entire reaction mass could be subjected to a constant shear rate. Recent work of Cioffi et al. [12] has shown a significant effect of shear rate on the reduction of gel effect in free radical polymerization. The rheokinetics of polyurethanes have been studied extensively by Lipshitz and Macosko [13], Richter and Macosko [14], Castro et al. [15], and Blake et al. [16]. They investigated the viscosity changes during various thermoplastic and thermosetting urethane polymerizations in Coutte rheometers and have found that the shear rate has no significant effect on the viscosity of the reaction mixture and hence on the extent of reaction at low values of viscosity ( $<100$  Pa.s) and shear rate ( $30\text{ s}^{-1}$ ). For a thermosetting polyurethane system however, Briscoe et al. [17] have observed an increase in viscosity build-up and a shorter gel time while increasing the shear strain.

The impingement mixing of reactants in the RIM process

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of polyurethanes has also been shown to be an effective parameter on the rate of reaction. The final conversion was increased as Reynolds number (Re) at the mixing nozzle increased up to a critical Re beyond which no further improvement could be seen [18, 19]. Finally, Lee and Lee [20] have examined the effect of mixing rate on the conversion profile of a nonlinear polyurethane formation in an adiabatic batch reactor. They modeled the interactions of mixing parameters, diffusion, and chemical reaction [20].

Malkin and Kulichikhin [21, 22] and Malkin et al. [23] have extensively studied the rheokinetic effects in processes of linear polymerization and three-dimensional oligomer curing. These authors have found that the changes in rheological properties during linear polymerization can be described by relationships based on treating a reactive mass as a polymer solution, as far as the newly formed polymer is soluble in reactive medium. Phase separation limits this approach and leads to some new rheological consequences such as change in the rate of viscosity growth. They showed that shearing influences the temperature of phase transition and kinetics of chemical reaction if it proceeds in heterogeneous conditions [22, 23].

In spite of the works mentioned above, there have been few fundamental studies on the quantified effect of shear rate on the kinetics of thermoplastic polyurethane formation. In this study we obtained the reaction kinetic constants of linear polyurethane systems at different shear rates and different temperatures. Two different TPU systems are investigated, in order to extra validate our conclusions indicating the influence of the shear rate on the polymerization kinetics. The results can particularly be useful in kinetic analysis and modeling of polyurethane reactions in extruders.

## THEORY

### Reaction Kinetics

Although the exact reaction mechanism of polyurethane formation is more complex, the kinetics of reaction of diisocyanate with dihydroxyl compound is often expressed successfully by a second-order rate equation [1, 2, 7, 24, 25]:

$$\frac{-d[NCO]}{dt} = k[NCO][OH] \quad (1)$$

where  $k$  is the kinetic constant (a function of catalyst concentration and temperature), and  $[NCO]$  and  $[OH]$  are the concentrations of isocyanate and hydroxyl groups, respectively. The number average molecular weight ( $M_n$ ), which can be considered as a measure of conversion, increases linearly with the reaction time for this system. In particular, for equal stoichiometry of functional groups, the dependency of the molecular weight on time is given by [24, 25]:

$$\bar{M}_n = M_0(1 + [NCO]_0 kt) \quad (2)$$

in which  $M_0$  is the average molecular weight of reactants, and the kinetic constant ( $k$ ) can be obtained from the slope of the molecular weight vs. time curve.

### Viscosity Function

The viscosity of a polymer liquid depends on several variables including shear rate, molecular weight, and temperature. The following correlation is quite reliable for dependence of viscosity on molecular weight of linear polymers:

$$\eta \propto M_w^\alpha \quad (3)$$

where the power  $\alpha$  is equal to 3.4 and 1, for higher and lower molecular weights, respectively. The transition between these two regimes happens at a critical value of molecular weight ( $M_c$ ) where entanglements begin to play an important role [26–28].

The viscosity of the polymerizing mixture increases with time as the urethane formation advances due to an increase in molecular weight. The time dependency of viscosity of oligourethanes can be expressed through an exponential function as shown below [29, 30]:

$$\eta(t) = \eta_0 e^{k_\eta t} \quad (4)$$

where  $\eta_0$  is the viscosity at  $t = 0$  and  $k_\eta$  is the rate constant for viscosity buildup. Taking the logarithm we get:

$$\ln \eta = \ln \eta_0 + k_\eta t. \quad (5)$$

Therefore, plotting  $\ln \eta$  against  $t$  should yield a straight line, the slope of which is the rate constant for the viscosity buildup.

## EXPERIMENTAL

### Materials

Two different linear polyurethane systems were used in this investigation. 4,4'-diphenyl methane diisocyanate (MDI) was reacted separately with a short diol as well as with a polyester polyol, leading to two extremes in the percent of hard segments (100% and 0%, respectively) in polyurethane structure. System I consisted of uncatalyzed reaction of MDI (Huntsman Polyurethanes, MW = 250 g/mol) with 1,4-butanediol (1,4-BDO; ICI, MW = 90 g/mol). In system II, a polyester polyol (Huntsman Polyurethanes) with molecular weight of 2200 g/mol and functionality of 2, was reacted with MDI. This reaction was catalyzed with 1% (by weight) of dibutyltin dilaurate (DBTDL; Aldrich).

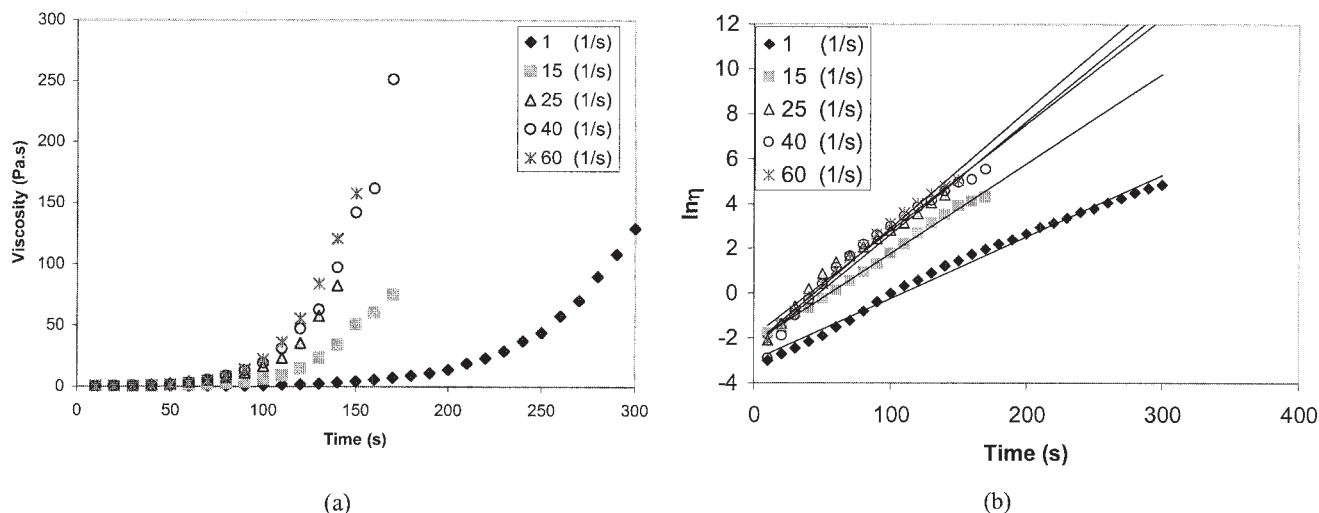


FIG. 1. Viscosity buildup at 85°C for system I at different shear rates (a) and their linear correlations for  $\ln \eta$  vs. time curves (b).  $\ln \eta = \ln \eta_0 + k_\eta t$ .

An equal stoichiometry of NCO and OH was used in both systems. The initial concentrations of isocyanate ( $[NCO]_0$ ) were  $5.88 \times 10^{-3}$  and  $8.16 \times 10^{-4}$  mol/g, for systems I and II, respectively.

Some experiments were repeated using 1,4-BDO and polyester that were dried under vacuum for a few hours before the reaction. No significant difference in the results was observed. MDI and catalyst were used as received.

#### Viscosity Measurements

The isothermal increase of viscosity during polyurethane formations were measured in a cone and plate rheometer (TA Instruments, Model AR-1000-N) with a 50-mm diameter aluminum cone and a cone angle of 2°. The temperature was precisely controlled using a Peltier Plate. The rheometer was provided with a solvent trap. The preweighed components were mixed for 30 s in a disposable beaker, and 0.7-ml of sample was transferred by syringe to the cone and plate. The small size of the sample reduced any nonisothermal effects due to heat of reaction.

The changes of viscosity with time for systems I and II were measured at different shear rates of 15, 25, 40, and 60 (1/s). The experiments were carried out at four temperatures of 50, 60, 85, and 100°C. At different times of reaction, the measurement was stopped and a sample was taken by rising the cone up, followed by immediately quenching the material in liquid nitrogen. In order to inactivate the still reactive isocyanate end-groups, samples were dissolved in a solution of dibutylamine (DBA) in tetrahydrofuran (THF), and were kept for GPC analysis.

In order to check the rheological effect of shear rate on the viscosity, several polyurethane samples with certain molecular weights were prepared by quenching the reaction mixture in THF/DBA solution at different reaction times. The solvent was then completely removed from samples

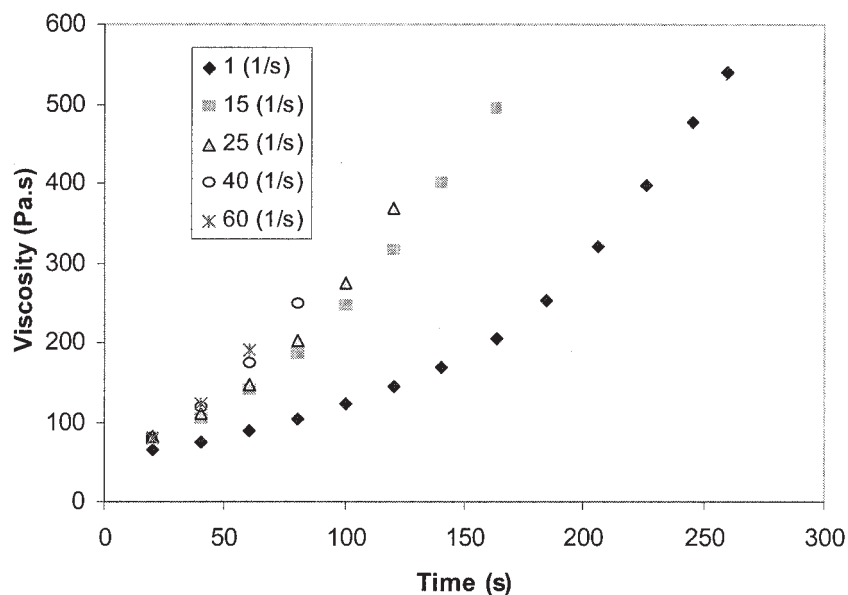
and the viscosity vs. shear rate experiments were carried out at different temperatures.

#### Molecular Weight Measurements

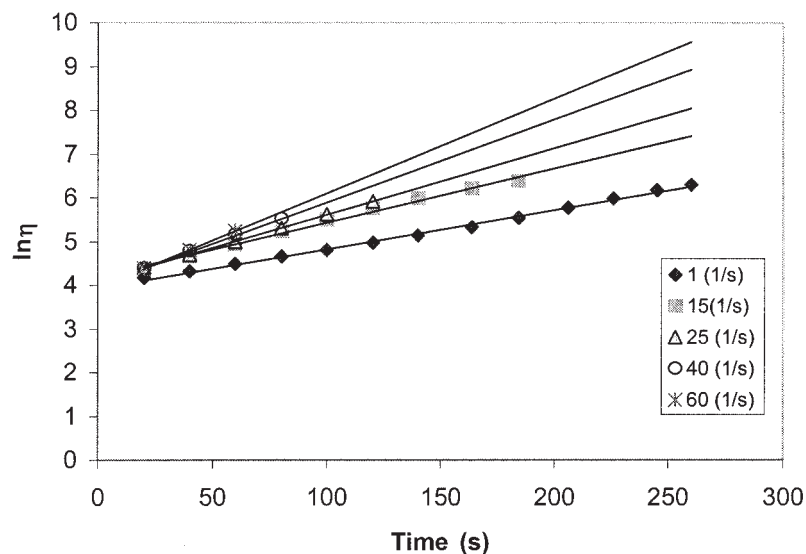
The molecular weights of samples were measured with a GPC system (Polymer Laboratories), which consisted of two 10- $\mu$ m Mixed-B columns and a refractive index detector. THF at a flow rate of 1.1 ml/min was used at 30°C as solvent. The GPC was calibrated with polystyrene standards. The samples were prepared in THF at a concentration of about 1–2 mg/ml. The molecular weight distribution was analyzed using Polymer Laboratories GPC-software.

## RESULTS AND DISCUSSIONS

Rheokinetic experiments have been performed at different temperatures and different shear rates both for system I and II. Two typical results of the viscosity buildup of reaction masses at 85°C are shown in Figs. 1 and 2. The viscosity vs. time data can be fitted with an exponential function trend as given in Eq. 3, independently of the operating condition. The results are in good agreement with the recent investigations of Sekkar et al. [29, 30] in which a similar exponential behavior was observed for polyurethane systems. The  $\ln \eta$  vs. time curves indicate a better linearity for system II in comparison with that of system I. According to Castro et al. [15], Malkin and Kulichikhin [22], and Malkin et al. [23], this may be attributed to different structures of these two polyurethane systems. While system II contains a homogeneous soft segment structure owing to a long-chain polyester, in system I, the reaction of short-chain diol and diisocyanate molecules leads to formation of hard urethane segments, which (due to hydrogen bonding) will aggregate as the reaction proceeds. This aggregation makes the oligomers less soluble in the rest of monomer mixture as



(a)



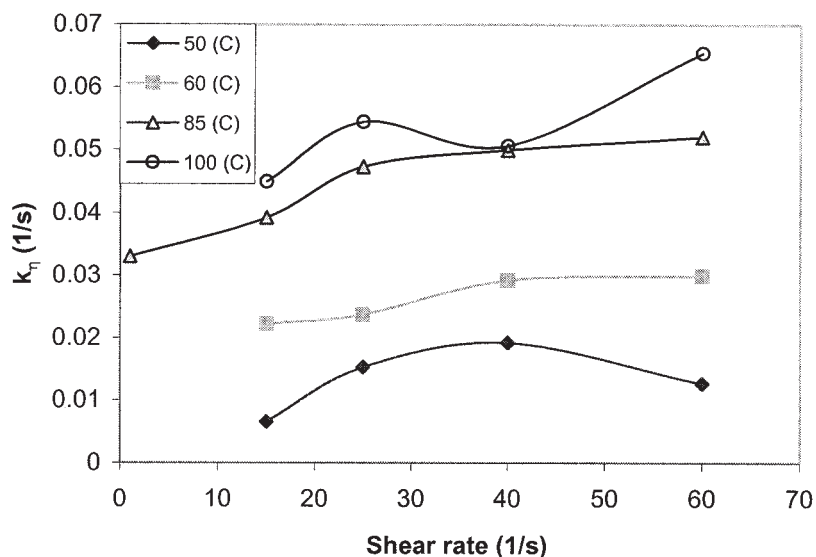
(b)

FIG. 2. Viscosity buildup at 85°C for system II at different shear rates (a) and their linear correlations for  $\ln \eta$  vs. time curves (b).  $\ln \eta = \ln \eta_0 + k_\eta t$ .

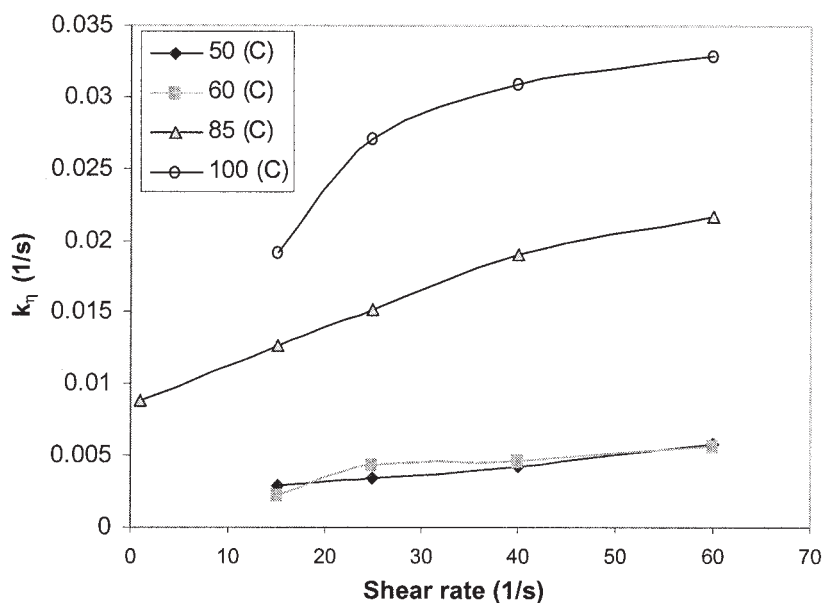
the hydrogen bonds between the urethane linkages are much stronger than the weak oligomer–monomer interactions [1, 2]. Thus, a heterogeneous reaction mixture will form in the gap between cone and plate in the rheometer. This can cause some small deviations in regular exponential trend of viscosity build-up of the reaction mixture.

The effect of shear rate on the viscosity changes at different temperatures can be observed in Fig. 3. The  $k_\eta$  values generally increase with shear rate and/or temperature. According to Eqs. 2–5, this can be attributed to the promotion of reaction kinetic that leads to formation of

higher molecular weight polymers at any time [26–28]. The increase in the rate of viscosity progress in the polymerizing mixture with the increase in shearing and temperature is in spite of the negative effects of these parameters on the viscosity from a purely rheological point of view. Lipshitz and Macosko [13] and Richter and Macosko [14], have found experimentally that the viscosity of cross-linking polyurethane systems is independent of the shearing at low viscosities and low shear rates. However, as Fig. 4 shows, shear-thinning behaviors were experimentally observed for both thermoplastic polyurethane systems at the range of



(I)



(II)

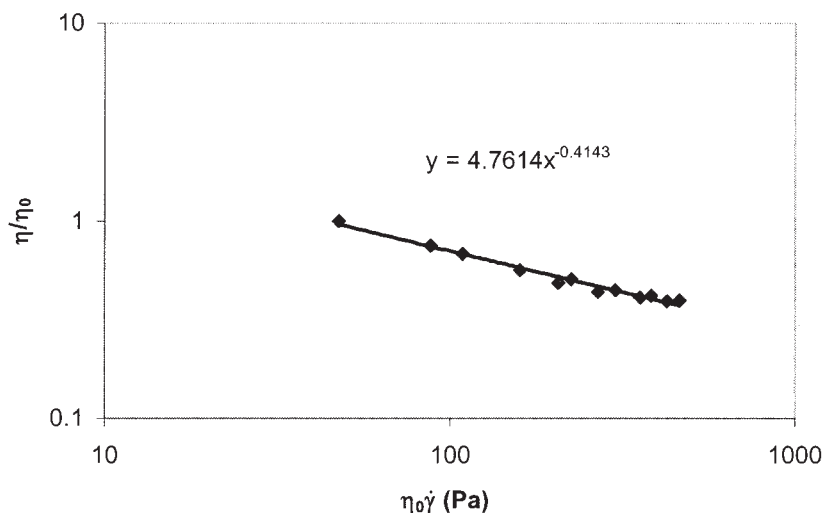
FIG. 3. Effect of shear rate on the kinetic constant for viscosity buildup at different temperatures for systems I and II. (Uncertainty in determination of  $k_\eta$  values: 5–15%.)

shear rates examined in this work. Normalization of the viscosity with respect to temperature allows us to investigate its dependency on shear alone. The ratio of apparent viscosity to the initial Newtonian viscosity ( $\eta_0$ ) becomes a temperature independent function of the product of the shear rate by the Newtonian viscosity, i.e., a function of the shear stress  $\tau$  only [26–28].

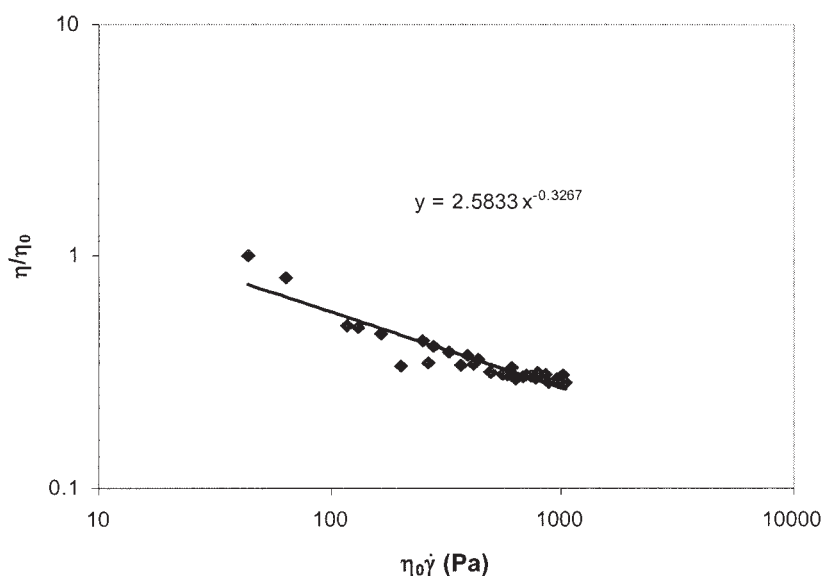
The pure influence of shear rate on the kinetics of formation of polyurethane systems are well understood from Fig. 5, in which the progress of number average molecular weight during the reaction time at various shear rates are typically given at 85°C for both systems. The higher the

shear rate imposed, the higher the molecular weight obtained at the same reaction time. The GPC measurements showed that the conversion of NCO groups in rheokinetic experiments for system I and II, starts from 51%  $\pm$  3% and 0.86%  $\pm$  1%, respectively, just after premixing of components, and ends at 77–88% and 90–98% at the final point, depending on the operating conditions.

The reaction kinetic constants are separately plotted vs. shear rate at different temperatures in Fig. 6. The promotion of reaction kinetics at high shear rate for these two TPU systems can be explained by two different arguments. In system I, the formation of stiff and polar urethane bonds



(I)



(II)

FIG. 4. Master viscosity curves for shear-thinning behavior of polyurethane systems I and II.

results in aggregation and crystallization of hard phase domains. The maximum concentration of rigid segments in this system acts as physical cross-linking in the polymerizing mixture that reduces the mobility of chains. Imposing high shear rate may align the polymer chains through dissociation of some rigid urethane segments and increase the mobility of polymer chains so that the diffusion and reaction of functional groups would be enhanced.

In system II, no aggregation of hard segments would occur. The critical molecular weight ( $M_c$ ) of this thermoplastic polyurethane can be estimated, using the group contribution approach described by Van Krevelen and Hoftyzer [28], to be 6856 g/mol. Since the polymerization mixture, even at the early stages of rheokinetic experiment, has an average molec-

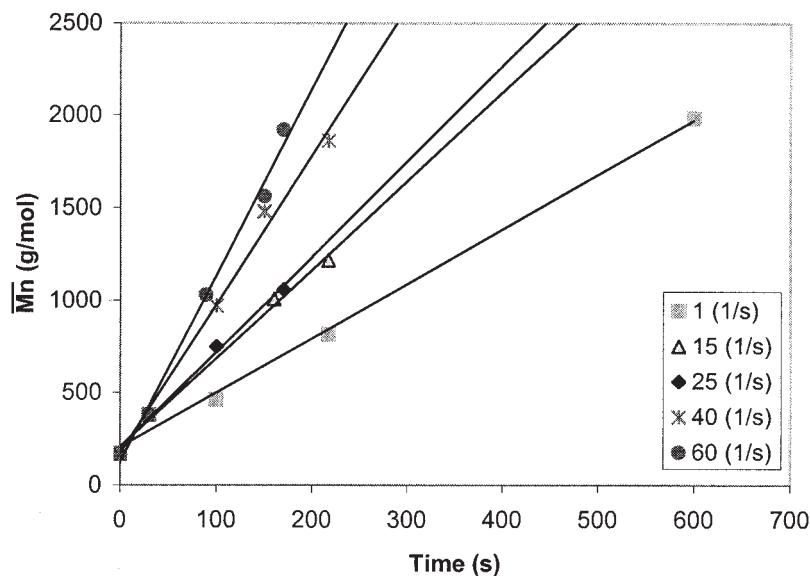
ular weight higher than the critical value, it is right to assume that the entanglements of polymer chains in system II are formed consequently. The shear induces elongation and orientation of long chain entangled macromolecules; therefore, the mobility of functional end-groups and catalyst molecules will increase, giving rise a higher reaction rate.

The effect of shear rate on the reaction kinetics is more significant at higher temperatures for both systems as shown in Fig. 6.

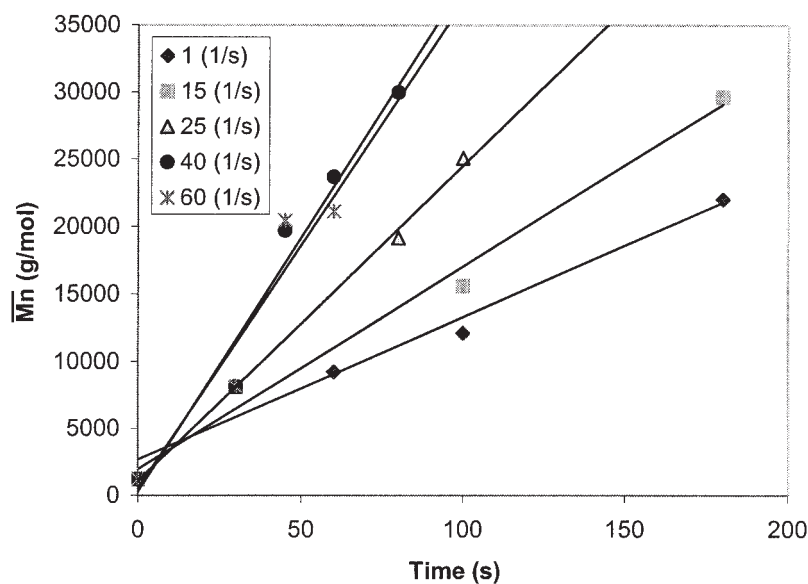
#### *Irregularity in Viscosity of System I at High Conversions*

In system I, the viscosity change of the reaction mass showed a highly irregular and irreproducible trend at high





(I)



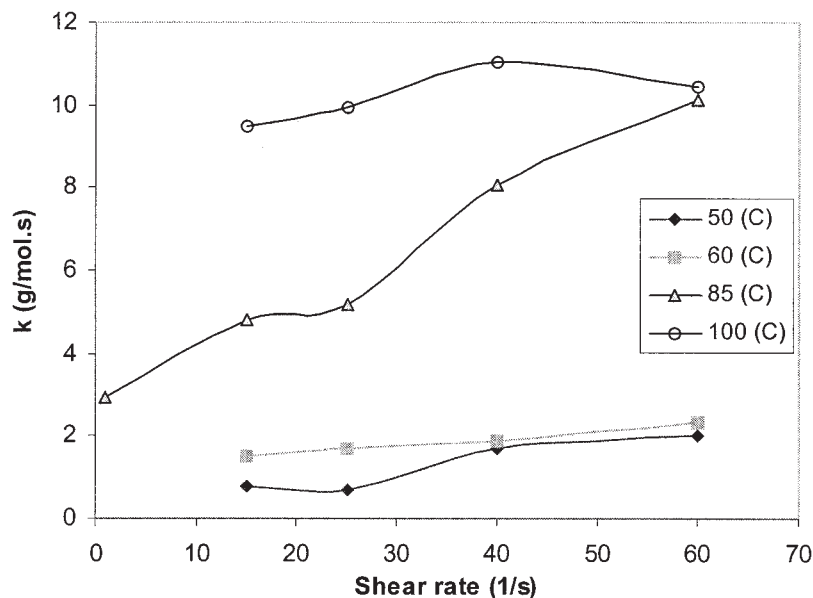
(II)

FIG. 5. Effect of shear rate on molecular weight increasing during the reaction time at 85°C (TPU systems I and II).

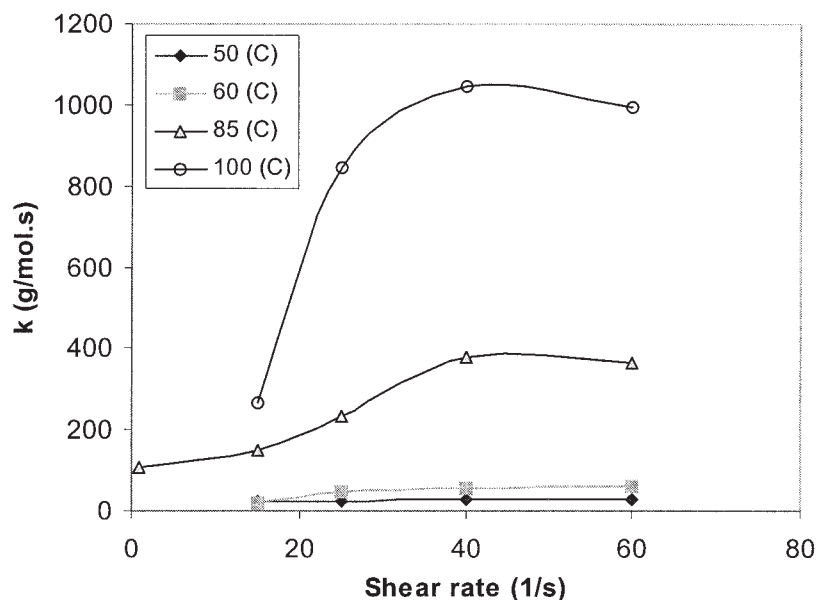
conversions. Figure 1 refers only to the part of the polymerization process during which the increase of viscosity with time has a regular trend. At higher conversions, the viscosity suddenly decreased and then showed a highly irregular behavior, as indicated in Fig. 7. Similar trends were observed in the experiments performed in a different rheometer (Brabender Co., Germany) with the same cone diameter and a cone angle of 3°. The viscosities at the onset of irregularity correspond to a range of conversions of about 77–88%, as obtained by GPC analysis.

The irregularity in viscosity at high conversions has also been reported by other authors for free radical polymerization and was attributed to phase separation [12, 21, 22, 31]. This explanation is much more reasonable for polyurethane system composed by MDI and BDO that contains 100% hard segment. As was mentioned before, at a certain point of polymerization, aggregation of hard urethane segments occurs due to hydrogen bonding [1, 2]. These aggregates are no longer soluble in the residual monomers at the reaction temperature and separates from the bulk phase, giving rise





(I)



(II)

FIG. 6. Effect of shear rate on the reaction kinetic constants at different temperatures (TPU systems I and II). (Uncertainty in determination of  $k$  values: 5–15%.)

to instability of the viscosity trend. This hypothesis is confirmed by the fact that no irregularity in viscosity build-up was observed for system II composed by MDI and polyester with 0% hard segments. The phase separation does not occur in this polyurethane system. The end points in viscosity curves of system II correspond to the upper reliable limit of shear stress of the rheometer.

The effect of shear rate on the onset of irregularity in viscosity of system I did not show any specific trend, most

likely due to the fact that the phase separation may begin in a relatively wide range of conversions.

## CONCLUSIONS

The change of viscosity with time during formation of linear polyurethanes can be modeled with an exponential function. The kinetic constant for viscosity buildup increases with shear rate due to promotion of reaction kinet-

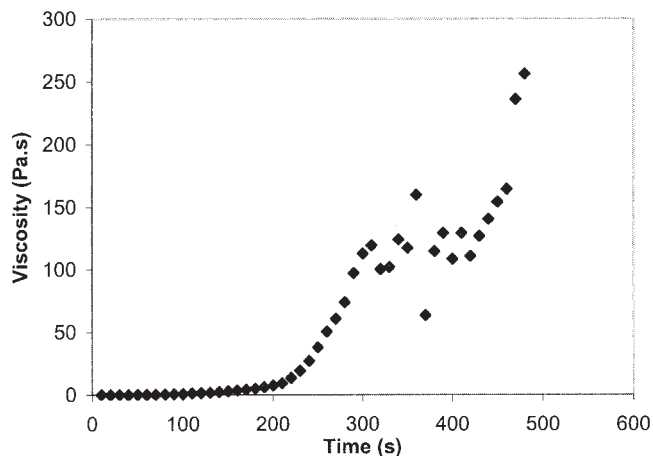


FIG. 7. A typical irregular trend of the viscosity at high conversions during polymerization of system I at 60°C and 40 (1/s).

ics. For MDI/BDO polyurethane with maximum hard segments, the shear may align the polymer chains through dissociation of some rigid urethane segments. In the case of an MDI/polyol system, the shear induces elongation and orientation of long chain entangled macromolecules. Hence, the shear enhances the mobility of polymer chains and diffusion of functional groups, so that the rate of polymerization is increased. It is also concluded that the irregularities in the viscosity buildup, while formation of MDI/BDO polyurethane at high conversions is due to phase separation of hard segments.

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## REFERENCES

1. Z. Wirpsza, *Polyurethanes*, Ellis Harwood, New York (1993).
2. C. Hepburn, *Polyurethane Elastomers*, 2nd ed., Elsevier Science, London (1992).
3. E. Broyer and C.W. Macosko, *Polym. Eng. Sci.*, **18**, 382 (1978).
4. G.G. Viola and W.R. Schmeal, *Polym. Eng. Sci.*, **34**, 1173 (1994).
5. K.J. Ganzeveld and L.P.B.M. Janssen, *Polym. Eng. Sci.*, **32**, 457 (1992).
6. A. Bouilloux and C.W. Macosko, *Ind. Eng. Chem. Res.*, **30**, 2431 (1991).
7. M.A. Semsarzadeh and A.H. Navarchian, *J. Polym. Eng.*, **23**, 225 (2003).
8. C.M. Thompson, *J. Polym. Sci.; Part A: Polym. Chem.*, **28**, 333 (1990).
9. P. Krol, *J. Appl. Polym. Sci.*, **57**, 739 (1995).
10. V. Sekkar, *J. Appl. Polym. Sci.*, **66**, 1795 (1997).
11. A. Kumar and S.K. Gupta, *Polymer*, **24**, 443 (1983).
12. M. Cioffi, A.C. Hoffmann, and L.P.B.M. Janssen, *Chem. Eng. Sci.*, **56**, 911 (2001).
13. S.D. Lipshitz and C.W. Macosko, *Polym. Eng. Sci.*, **16**, 803 (1976).
14. E.B. Richter and C.W. Macosko, *Polym. Eng. Sci.*, **20**, 921 (1980).
15. J.M. Castro, C.W. Macosko, and S.J. Perry, *Polym. Commun.*, **25**, 83 (1984).
16. J.W. Blake, W.P. Yang, R.D. Anderson, and C.W. Macosko, *Polym. Eng. Sci.*, **27**, 1237 (1987).
17. B.J. Briscoe, S.M. Richardson, and M.B. Khan, *Plast. Rub. Proc. Appl.*, **10**, 65 (1988).
18. L.J. Lee, J.M. Ottino, W.E. Ranz, and C.W. Macosko, *Polym. Eng. Sci.*, **20**, 868 (1980).
19. P. Kolodziej, C.W. Macosko, and W.E. Ranz, *Polym. Eng. Sci.*, **22**, 388 (1982).
20. Y.M. Lee and L.J. Lee, *Int. Polym. Proc.*, **1**, 144 (1987).
21. A.Ya. Malkin and S.G. Kulichikhin, *Rheokinetics*, Huthig & Wept Verlag, New York, (1996).
22. A.Ya. Malkin and S.G. Kulichikhin, *Die Makromol. Chem., Macrom. Symp.*, **68**, 301 (1993).
23. A.Ya. Malkin, S.G. Kulichikhin, D.N. Emel'yanov, I.E. Smetanina, and N.V. Ryabokon, *Polymer*, **25**, 778 (1984).
24. G. Odian, *Principles of Polymerization*, 3rd ed., John Wiley, New York (1991).
25. P. Rempp and E.D. Merrill, *Polymer Synthesis*, Huetig and Webf, New York (1986).
26. C.D. Han, *Rheology in Polymer Processing*, Academic Press, New York (1976).
27. Q.W. Lu, M.E.H. Hernandez, and C.W. Macosko, *Polymer*, **44**, 3309 (2003).
28. D.W. Van Krevelen, and P.J. Hoftyzer, *Properties of Polymers*, Elsevier Science, Amsterdam (1976).
29. V. Sekkar, S. Venkatachalam, and K.N. Ninan, *Eur. Polym. J.*, **38**, 169 (2002).
30. V. Sekkar, K.A. Devi, and K.N. Ninan, *J. Appl. Polym. Sci.*, **79**, 1869 (2001).
31. M. Cioffi, A.C. Hoffmann, and L.P.B.M. Janssen, *Nonlinear Anal.*, **47**, 897 (2001).